

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 728 796 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
07.07.1999 Bulletin 1999/27

(51) Int Cl.⁶: **C08J 3/20, C08J 3/12,
C08L 23/00, C08K 5/14,
B29C 67/24, B29C 47/10**

(21) Application number: **96301120.0**

(22) Date of filing: **20.02.1996**

(54) **Process for improving processability of ultra low melt viscosity polymer**

Verfahren zur Verbesserung der Verarbeitbarkeit von Polymeren mit ultraniedriger Schmelzviskosität

Procédé d'amélioration de la transformabilité de polymère à ultrafaible viscosité à l'état fondu

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE

• **McCullough, J.R. James Douglas**
Houston, Texas 77079 (US)

(30) Priority: **21.02.1995 US 395365**

(74) Representative:
Ellis-Jones, Patrick George Armine
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(43) Date of publication of application:
28.08.1996 Bulletin 1996/35

(73) Proprietor: **SHELL OIL COMPANY**
Houston Texas 77002 (US)

(72) Inventors:
• **Hwo, Charles Chiu-Hsiung**
Sugar Land, Texas 77478 (US)
• **Ma, Chin-Yuan George**
Sugar Land, Texas 77479 (US)

(56) References cited:
WO-A-87/06944 WO-A-91/16716
GB-A- 2 100 268 US-A- 4 451 589
US-A- 4 721 589 US-A- 4 897 452
US-A- 5 264 493

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 728 796 B1

Description

[0001] This invention relates to an improved process for the manufacture of pellets of ultra low melt viscosity polyolefin, which process involves the degradation or "cracking" of olefin polymers in the presence of free radical generators in a pelletizing extruder, especially in relation to the pelletizing characteristics of the degraded polymers.

[0002] It is known that ultra low melt viscosity polymers are useful for the production of a variety of products such as adhesives, sealants, coatings, non-woven fabrics by melt blown fiber processes, injection-molded components made at a high rate, etc. An ultra low melt viscosity polymer has a melt viscosity of about 300 Pa.s (300,000 centipoise (hereinafter "cps")) or lower. The melt viscosity of an ultra low melt viscosity polymer can be as low as 0.5 Pa.s (500 cps) or smaller.

[0003] However, it is difficult to use a polymerization process to obtain directly polymers of a very low melt viscosity. Due to their particular nature, such polymers can require complex and costly operations, primarily in relation to the use of solvents, especially operations of separating the polymers from the solvents in which they are prepared. Thus, it has been proposed to prepare olefinic polymers with a relatively high melt viscosity according to usual polymerization processes and then to subject these polymers to a thermomechanical degradation treatment in the presence of a free radical generator, under such conditions that the melt viscosity of these polymers decreases to the desired value. In theory, during this treatment, the thermal decomposition of the free radical generator, such as a peroxide, can cause the macromolecular chains of the olefinic polymer to break and thus the melt viscosity of the polymer to decrease.

[0004] As used herein, a high melt viscosity polymer is defined as a polymer having a melt viscosity 1 kPa.s (1,000,000 cps) or more; and an ultra low melt viscosity polymer is a polymer having a melt viscosity of about 300 Pa.s (300,000 cps) or lower. A polymer with a melt viscosity of about 300 Pa.s (300,000 cps) will have a melt index of approximately 100 dg/min, and is generally regarded as an ultra high melt flow rate polymer with an ultra high melt index. As used herein, the melt viscosity is measured by Brookfield Viscometer using ASTM D2556 at 177°C (350°F), unless otherwise specified e.g. as measured at 135°C (275°F). As used herein, the melt flow rates or melt indices are measured by ASTM 1238 Condition E at 190°C and 2.16 g wt.

[0005] The pelletization of thermoplastic materials is of considerable importance for many applications. Pellets, unlike ingots or bars, readily flow in measuring and dispensing apparatuses and the size of pellet charges can be readily controlled to small tolerances. Moreover, unlike powders, they do not form dust and are not ingested by persons working with them. Thus, they provide a highly convenient form for the packaging, storage and use of many thermoplastic polymers.

[0006] It is known to carry out the thermomechanical degradation treatment in the presence of a free radical generator in an extruder, either during pelletization of the polymer or during the conversion of the pellets into finished articles. However, when the intention is to produce finished articles from, for example, butylene and/or propylene polymer with very low melt viscosity, i.e. very high melt index, it can be difficult to carry out this degradation treatment effectively. When the degradation treatment is carried out in a pelletizing extruder, the polymer leaving the extruder becomes so fluid and so soft that it is difficult or even impossible to cut into pellet form. Moreover, the pellets consisting of these polymers of very high melt index can be sticky and tend to agglomerate, making handling very difficult.

[0007] Attempts to pelletize ultra low melt viscosity polyolefins cracked by conventional processes result in an excess amount of non-uniform or malformed pellets. These pellets are undesirable since they tend to bridge in pellet feed hoppers and to block pellet conveying systems. Further, significant amounts of malformed pellets alter the bulk density of the pellet stock which causes feeding problems in the extrusion line and which may result in voids in the final product. In addition to malformed pellets, trashouts occur frequently during production of ultra low melt viscosity polyolefins. Trashouts are extruder shutdowns resulting from polymer buildup on the rotating knives.

[0008] The user of the pellets, i.e. the converter, is generally someone other than the manufacturer of the polymers and of the pellets. When the converter employs this degradation treatment during the conversion of the pellets into finished articles, he must modify and adapt the extruders or other converting devices and the conditions of their use, in order to effectively process each type of pellet. In particular, he must equip the extruders or other converting equipment with a device for introducing and metering the free radical generator, while satisfying safety constraints due to the thermal instability of these materials. It has been observed that when this degradation treatment is carried out with a polymer which is not in the form of a powder but in the form of pellets, the dispersion of the free radical generator in the polymer may be relatively more difficult and the lack of homogeneity of the mixture may result in local excessive degradation of the polymer.

[0009] The users of the pellets usually mix the pellets in appropriate equipment with additional ingredients such as additives, other polymers, and antioxidants to form a blend in its molten state before converting the mixture containing the pellets into finished articles. Thus, the viscosity of the pellets must be sufficiently low so that the blending or mixing operation can be successfully conducted without causing mechanical breakdown of the mixing stirrer because of the high shear resistance from the molten mixture.

[0010] It is therefore desirable to crack the polymer during the extrusion pelletization stage as much as possible to

meet the melt viscosity specification required by the end users, while at the same time stay within the melt viscosity range in which cracked polymer can easily be mechanically cut into non-sticky uniform pellets by the pelletizer.

[0011] It is also desirable to control the consistency of the degree of degradation in the extruder to have a narrow molecular weight distribution of the polymer in the pellets to prepare pellets of a quality which is as constant as possible. It is further desirable to control the constancy of the concentration of the live or intact, i.e. unreacted, free radical generators in the pellets. Such reproductability in the manufacture of the pellets advantageously reduces the need for the end users, the converters, to constantly change the settings of the converting equipment intended to convert the pellets into finished articles.

[0012] U.S.-A- 4,451,589 proposes a degradation process wherein greater than about 50% added peroxide remains available for further degradation after pelletizing. The peroxide can be added either prior to or during the extrusion process. However, the proposed single point addition of large amount of peroxide often leads to lack of control of the consistency of the degree of degradation and thus a large percentage of recoverable and unrecoverable products which do not meet the blending and/or shipping specifications.

[0013] U.S.-A- 4,897,452 proposes a degradation process involving adding to the polymer two free radical generators, G1 and G2, the half-life of G2 being at least 20 times longer than that of G1 at the pelletizing temperature. This process requires the use of G2 with a relatively long half life. The process has the disadvantage of requiring high temperature and/or prolonged heating during the conversion of the pellets into finished articles by the converters or end users in order to completely decompose the G2 free radical generators.

[0014] Thus, a need has been demonstrated for a process of degrading a polyolefin, producing polymer pellets of a constant quality, including constancy in viscosity, in a reproducible manner, while minimizing the viscosity of the polymer to meet the viscosity specification required by the customer, at the same time being easily cut into non-sticky pellets without excessive free radical prodegradant, and when heated undergoes further degradation producing a ultra low melt viscosity polymer without excessive heating.

[0015] The present invention provides a process for making polymer pellets containing unreacted free radical generator which can be degraded upon thermal treatment to form an ultra low melt viscosity olefin polymer (referred to hereafter as a polyolefin) having a melt viscosity up to, typically from about 0.5 Pa.s (500 cps) to, about 300 Pa.s (300,000 cps) measured by Brookfield Viscometer using ASTM D2556 at 177°C (350°F) which process comprises:

- (1) feeding an olefinic polymer feedstock having a melt index of from about 0.1 or 0.2 to about 100 dg/minute measured by ASTM 1238 Condition E at 190°C and 2.16 g wt to a main extruder,
- (2) determining the amount (x) of free radical generator required to degrade said polyolefin from step (1) in said main extruder, under the temperature(s) and residence time existing in said main extruder, to a polymer having a viscosity which is (i) sufficiently high to allow easy pelletization by pelletizer into tractable uniform non-sticky pellets with less than 5%, preferably less than 2% pellet agglomerates, and (ii) sufficiently low to allow blending without causing mechanical breakdowns of the mixing device by end user of the pellets;
- (3) determining amount of loss (y) of unreacted free radical generator during extrusion;
- (4) determining the total amount (z) of free radical generator required for degradation and loss in the main extruder by adding the amount (x) to the amount (y), wherein $z=x+y$;
- (5) adding said free radical generator in an amount from about 0.7 z to about 1.2 z either to (i) the first half section of the main extruder or (ii) said polymeric feedstock to form a first mixture;
- (6) cracking said first mixture in said main extruder under heat;
- (7) adding a second mixture comprising (i) from about 0.1 to about 100 wt% of a free radical generator, and (ii) from about 0 to about 99.9 wt% of said polymeric feedstock into the second half section of the main extruder, optionally through a side-arm extruder, to form a third mixture;
- (8) passing said third mixture exiting the end of the main extruder to a pelletizer to form pellets;

wherein said second mixture is added in step (7) in an amount which provides sufficient unreacted free radical generator in the pellets produced from step (8) for subsequent decomposition and cracking of the polymer in the pellets to form a polymer having from about 0.5 Pa.s (500 cps) to about 300 Pa.s (300,000 cps); and

wherein the half life of the free radical generator used in step (5) is within about 0.1-1.0 times the half life of the free radical generator used in step (7).

[0016] The accompanying drawing, Figure 1, represents diagrammatically one general arrangement of apparatus for carrying out the process. Accessories such as valves, pumps and control instruments not necessary for the purpose of understanding the present invention are not (all) shown.

[0017] The present invention involves a process of extrusion degradation of a polyolefin to form a degraded polymeric melt, which can be easily cut into non-sticky polymeric pellets containing unreacted free radical generator which can be degraded upon thermal treatment to form an ultra low melt viscosity polyolefin. Applicants have unexpectedly found that the process of the present invention can produce pellets of a constant quality, including constancy in viscosity

through consistency of the degree of degradation as well as improved control of the constancy of the concentration of unreacted free radical generators in the pellets, while the viscosity of the polymer is minimized to meet the viscosity specification required by the end users of the pellets to allow blending with ease without mechanical breakdowns of the mixing device.

[0018] The present invention is applicable to the processing of waste polymer material to permit reuse in various applications. It will be apparent to one skilled in the art, optimum operating conditions and concentrations will vary depending upon the properties of the polymer being used and the ultimate properties desired by the end users of the pellets.

[0019] The present process is suitable for cracking and pelletizing of any olefin polymer, preferably polymers of alpha-monolefins of three to eighteen carbon atoms having a melt indices of from about 0.2 to about 100 dg/minute, more preferably from about 0.2 to about 50 dg/minute, still more preferably from about 0.2 to about 20 dg/minute. Polymers with melt indexes of less than 20 dg/minute are generally regarded as low melt flow rate polymers. The polyolefin can be highly crystalline, semicrystalline, elastomeric, relatively amorphous, or essentially amorphous. Illustrative examples of the suitable polyolefins include butene-1 homopolymer, butene-1 copolymer, butene-1-ethylene copolymer, butene-1-propylene copolymer, propylene homopolymer, propylene copolymers, ethylene copolymers, and mixtures thereof, etc. A specific embodiment uses butene-1-ethylene copolymer made of from about 2 wt% to about 8 wt% of ethylene and from about 92 wt% to about 98 wt% of butene-1 having a melt index from about 0.1 to about 3.0 dg/min. Another specific embodiment uses a mixture of a butene-1 homopolymer or copolymer (hereinafter "homo (co) polymer") with a propylene homo(co) polymer. Still another specific embodiment uses a mixture of butene-1 homo (co) polymer, propylene homo(co) polymer, and less than about 25 wt% of ethylene homo(co) polymer.

[0020] In accordance with the present invention, referring to the accompanying figure a polyolefin feedstock, typically produced from a reactor, is introduced into a main extruder. The main extruder is generally a device for mixing and heating a polymer mixture. Suitable extruders include a single screw extruder and a twin screw extruder. Suitable extruders typically are from about 125 cm (50 inches) to about 2540 cm (1000 inches), preferably from about 510 cm (200 inches) to about 1270 cm (500 inches), and more preferably from about 635 cm (250 inches) to about 1020 cm (400 inches) in length. The residence time for the polymeric feedstock in the main extruder is typically from about 30 seconds to about 20 minutes, preferably from about 2 minutes to about 6 minutes, more preferably from about 3 minutes to about 5 minutes.

[0021] The extruder typically has a plurality of heating zones and is operated typically through a plurality of stages. The set temperatures of the heating zones will vary depending upon the properties of the polymers and the free radical generators, including the half-life of the free radical generator at operating temperatures. It is to be noted that during the extrusion process, a substantial amount of heat is often generated from shear heating and cracking reaction. Thus, the temperature of the polymeric melt in the extruder may be substantially higher than the temperature set in the heating zone(s) at the barrel of the screw, and may also be substantially higher than the actual zone temperature readings in the extruder. Further, the actual zone temperature readings in different stages of the extruder may also be higher than the temperatures set at the heating zones. Non-limiting examples of the temperatures set for the heating zones include from about 32°C (90°F) to about 260°C (500°F), specifically from about 66°C (150°F) to about 191°C (375°F), more specifically from about 82°C (180°F) to about 177°C (350°F).

[0022] A free radical generator, or a mixture of free radical generators, is typically added to the main extruder at the first half section of the main extruder, preferably at the first one-third section of the main extruder, and more preferably at the first one-quarter section of the main extruder.

[0023] In a specific embodiment the amount (z) of the free radical generator added at the first one-half section of the extruder is the sum of the amount x required for cracking in the main extruder and the amount of y which is the amount of free radical generator lost during the extrusion process. The amount x is the amount of the free radical generator (s) required to degrade the polyolefin feedstock in the main extruder, under temperature(s) and residence time of the main extruder, to a polymer having a viscosity in a range which meets at least two criteria: (1) the viscosity must be sufficiently high to allow easy pelletization by the pelletizer into tractable uniform non-sticky pellets with less than 5%, preferably less than 2 wt%, more preferably less than 0.5 wt% pellet agglomerates, and the frequency of extruder shutdowns resulting from polymer buildup on the rotating knives of the pelletizer is minimized; and (2) the viscosity of the polymer after degradation in the main extruder must be sufficiently low to allow blending without causing mechanical breakdowns of the mixing device by the end users of the pellets.

[0024] Optionally, the main extruder may contain one or more vent(s) for ventilating the side products produced from the cracking process. The vent(s) are located in the main extruder at a position after the injection point of the first free radical generator(s) and prior to the last injection point of the free radical generator(s). A portion of the free radical generator, especially when it is a liquid with a low boiling point, may evaporate from the vent(s) and resulting in the loss of free radical generators. The loss of the free radical generators from the vent(s) is in the range from about 0 wt% to about 60 wt%, specifically from about 10 wt% to about 50 wt%, more specifically from about 25 wt% to about 35 wt%, still more specifically about 33 wt%.

[0025] The amount (y) of free radical generator lost during the extrusion process, including the ventilations through the vent(s), can be determined by adding a predetermined amount of free radical generator(s) to a polymeric feedstock in an extruder with vent(s) open and determining the concentration of the free radical generator(s) contained in the polymeric mixture exiting the extruder, e.g. using gas liquid chromatography; repeating the same process with vent(s) closed; and determining the difference of the concentration of the free radical generator(s) contained in the polymeric mixture exiting the extruder.

[0026] The total amount (z) of free radical generator required for degradation and loss in the main extruder can be determined by adding x to y, i.e. using the equation: $z=x+y$.

[0027] In a specific embodiment of the present invention, free radical generator(s) in an amount from about 0.5 to about 1.5 time(s), preferably from about 0.7 to about 1.2 time(s), more preferably from about 0.9 to about 1.1 time(s) of z is added to the first one-half section of the main extruder. It can be added in one single injection, or in a plurality of injections.

[0028] The polymeric feedstock in combination with the free radicals added in the first stage of the main extruder is subsequently cracked in the extruder. As a specific embodiment at least 70%, preferably at least 80%, more preferably at least 90% of the free radical generators injected in the first half section of the extruder are decomposed, reacted or lost before reaching the exit of the main extruder.

[0029] Applicants have found by surprise that the present invention, by the controlled addition of the free radical generators in the first section of the extruder, in combination with the controlled addition of free radical generators in the last section of the extruder, produces polymer pellets with improved constancy in viscosity, with a higher percentage of prime pellets produced which meets the viscosity specification required by the end user.

[0030] A second portion of free radical generator(s) is added into last one-half section, preferably the last one-third section, more preferably the last one-quarter section, even more preferably immediately before the exit of the main extruder. Again, this can be added in one single injection, or in an incremental multiple injections. The free radical generator(s) can be added directly to the main extruder, or it can be added in the form of a mixture (masterbatch), e.g. comprising (i) from about 0.1 to about 100 wt% of free radical generator(s), and (ii) from about 0 to about 99.9 wt% of the polymeric feedstock. As a specific embodiment, the free radical generator(s) is added in a masterbatch containing from about 1 wt% to about 10 wt%, more specifically from about 1.5 wt% to about 2.5 wt% of free radical generator(s) to the mixture. The masterbatch can be added to the main extruder directly. In a specific embodiment of the present invention, the masterbatch containing the free radical generator(s) is first extruded in a side-arm extruder, optionally under heat, to be homogenized before the addition to the main extruder.

[0031] In a specific embodiment the masterbatch is added to the main extruder so that the master-batch is mixed with the polymeric melt in the main extruder in a ratio from about 1:19 to about 1:1, more specifically from about 1:9 to about 1:3, even more specifically from about 1:5 to about 1:6. The residence time of the material in the side-arm extruder ranges from about 10 seconds to about 2 minutes, specifically from about 20 seconds to about 1 minute, more specifically from about 30 seconds to about 45 seconds. The side-arm extruder primarily provides a convenient means for introducing the free radical generator via masterbatch to the main extruder. Since the residence time in the side-arm extruder is very short and the shear heating is very low due to its special design, the decomposition of the free radical generator in the side-arm extruder is thus minimal.

[0032] The second portion of the free radical generator(s) is added in an amount which provides sufficient amount of unreacted free radical generator(s) in the pellets available for subsequent decomposition and cracking of the polymer in the pellets to form an ultra low melt viscosity polymer having from about 0.5 Pa.s (500 cps) to about 300 Pa.s (300,000 cps), preferably from about 3 Pa.s (3,000 cps) to about 150 Pa.s (150,000 cps), and more preferably from about 6.5 Pa.s (6,500 cps) to about 105 Pa.s (105,000 cps).

[0033] The addition of the second portion of the free radical generator(s) at the last stage of the extruder, specifically very close to the end of the extruder, unexpectedly results in improved control of the constancy of the concentration of the unreacted free radical in the pellets. Such reproducibility in the manufacture of the pellets advantageously reduces the need for the end users of the pellets to constantly change the settings of the converting equipment intended to convert the pellets into finished articles.

[0034] In a specific embodiment the 1 hr. half life temperatures, i.e. the temperature at which the time required for one-half of the free radical generator to decompose is one hour, of the free radical generators suitable for use in the present process are in the range from about 110°C to about 150°C. Such half lives properties advantageously provide sufficient cracking efficiency in the extrusion step and during the conversion of the pellets into finished articles, and avoid prolonged heating at a high temperature otherwise required during the conversion step by the end users.

[0035] Examples of suitable peroxides include the peroxides listed in TABLE 1 below.

TABLE 1

CHEMICAL NAME OF PEROXIDE	1 HR. HALF LIFE TEMP (°C)
t-butylperoxy-maleic acid	110
OO-t-butyl O-isopropyl monoperoxycarbonate	119
OO-t-butyl O-(2-ethoxyl) monoperoxy-carbonate	121
2,5-dimethyl 2,5-di(benzoylperoxy) hexane	118
OO-t-amyl O-(2-ethylhexyl) mono peroxy carbonate	117
TABLE 1 - Cont'd	
t-butylperoxy acetate	120
t-amyl peroxy acetate	120
t-butylperoxy benzoate	125
t-amyl peroxy benzoate	121
di-t-butyl diperoxy-phthalate	123
dicumyl peroxide	135
2,5-dimethyl-2,5-di(t-butylperoxy) hexane	138
t-butyl cumyl peroxide	142
α-α-bis(t-butylperoxy) diisopropylbenzene	137
di-t-butyl peroxide	149
2,5-dimethyl-2,5-di(t-butylperoxy) hexyne-3	149
n-butyl-4,4-bis(t-butylperoxy) valerate	129
1,1-di(t-butylperoxy) 3,3,5-trimethyl cyclohexane	112
1,1-di (t-butylperoxy) cyclohexane	112
1,1-di-(t-amylperoxy) cyclohexane	112
2,2-di (t-butylperoxy)butane	122
ethyl-3,3,-di (t-butylperoxy) butyrate	135
2,2-di (t-amylperoxy) propane	128
ethyl 3,3-di(t-amylperoxy) butyrate	132

[0036] The chemical composition of the free radical generator(s) injected to the first one-half section (or the first stage) of the extruder and that added to the last one-half (or the last stage) can be identical. In the alternative, two different free radical generators or mixtures of free radical generators can be added, with the provision that the half life of the free radical generator(s) used in the first injection(s) in the first one-half section of the extruder is within about

0.1 to about one times the half life of the free radical generator(s) injected into the last one-half section of the extruder.

[0037] At the exit of the extruder, the polymeric melt is continuously extruded through the orifices of the die plate into water filled housing. The polymeric melt is pelletized into pellets using any convenient means known in the art. In one embodiment, the molten polymer from the extruder is fed to a pelletizer in which the polymer flows through the holes of the die plate and cut by knives into pellets, which are immediately quenched by chill water in the crystallization tank. In another embodiment, the polymeric strands are extruded and while immersed in water, they are cut into short lengths or pellets and are then quickly cooled by the water and carried in suspension from the housing to a collection station.

[0038] The polymer in the pellets produced will generally have a viscosity from about 50 Pa.s (50,000 cps) to about 500 Pa.s (500,000 cps), preferably 100 Pa.s (100,000 cps) to about 500 Pa.s (500,000 cps), more preferably from about 200 Pa.s (200,000 cps) to about 500 Pa.s (500,000 cps) measured by Brookfield Viscometer using ASTM D2556 at 135°C (275°F); and a melt viscosity of from about 0.5 Pa.s (500 cps) to about 300 Pa.s (300,000 cps), preferably from about 3 Pa.s (3,000 cps) to about 150 Pa.s (150,000 cps), and more preferably from about 6.5 Pa.s (6,500 cps) to about 105 Pa.s (105,000 cps) measured by Brookfield Viscometer using ASTM D2556 at 177°C (350°F). The melt viscosity measured at 177°C (350°F) reflects the viscosity of the pellets after being fully cracked, and that measured at 135°C (275°F) reflects the viscosity of the pellets produced from the extrusion pelletization which provides an indication of the processability of the pellets, such as ease of pelletization and ease of blending with other ingredients at a selected temperature by the end users. The melt viscosity of the polymeric melt and/or pellets can be measured by a melt flow meter located at or after the third stage of the extruder. The melt viscosity can be adjusted, e.g. by changing the temperature settings of the heating zones, and adjusting the concentrations of the free radical generator(s) injected.

[0039] In a specific embodiment a process is provided for making polymer pellets comprising unreacted 2,5-dimethyl-2,5-di(t-butylperoxy) hexane which can be degraded upon thermal treatment to form ultra low melt viscosity butene-1-ethylene copolymer having a melt viscosity measured by Brookfield Viscometer using ASTM D2556 at 177°C (350°F) of from about 3 Pa.s (3,000 cps) to about 150 Pa.s (150,000 cps), preferably from about 6.5 Pa.s (6,500 cps) to about 105 Pa.s (105,000 cps). The process comprises the steps of feeding a polymeric feedstock comprising a butene-1-ethylene copolymer consisting essentially of (i) from about 92 wt% to about 98 wt% of butene-1 and (ii) from about 2 wt% to about 8 wt% of ethylene having a melt index of from about 0.1 to about 3.0 dg/min measured by ASTM 1238 Condition E at 190°C and 2.16 g wt to a main extruder through a feeding device, wherein total residence time for the polymeric feedstock in the main extruder from the feeding device to end of the main extruder ranges from about 2 minutes to about 6 minutes. In this specific process, from about 800 to about 3500 ppm of 2,5-dimethyl-2,5-di(t-butylperoxy) hexane is added to the polymeric feedstock (i) into about first one third section of the main extruder, or (ii) prior to the feeding of said polymeric feedstock to said extruder to form a first mixture. This first mixture is cracked in the main extruder under heat. Subsequently, a second mixture comprising (i) from about 0.1 wt % to about 100 wt % of 2,5-dimethyl-2,5-di(t-butylperoxy) hexane and (ii) from about 0 to about 99.9 wt% of said polymeric feedstock is added into the last one third section of the main extruder to form a third mixture, which is passed through the exit of the extruder to a pelletizer to form pellets. The degraded butene-1-ethylene copolymer in the polymer pellets has a viscosity of from about 200 Pa.s (200,000 cps) to about 500 Pa.s (500,000 cps) measured at 135°C (275°F) using ASTM D2556 and from about 3 Pa.s (3,000 cps) to about 150 Pa.s (150,000 cps) measured at 177°C (350°F) using ASTM D2556. The second mixture containing peroxide is added to the main extruder in such amount that the polymer pellets produced comprises from about 2900 to 3500 ppm of unreacted peroxide. Optionally, the second mixture is passed through a side-arm extruder prior to the addition to the last one third section of the main extruder. Optionally, the main extruder comprises at least one vent at a position after the position at which the first portion of 2,5-dimethyl-2,5-di(t-butylperoxy) hexane is added to the main extruder and before the second mixture is added to the main extruder in the last stage of the extruder.

[0040] The following Examples further illustrate the present invention.

ILLUSTRATIVE EMBODIMENT I

PART I: FEEDSTOCK POLYMER

[0041] Butene-1-ethylene copolymer containing 5.5 wt% of ethylene having a melt index of about 0.2-0.4 dg/min was produced from a polymerization reactor by polymerizing butene-1 with ethylene using a titanium trichloride catalyst containing as cocatalyst diethylaluminum chloride/diethyl aluminum iodide. The polymer produced from the reactor is first transferred to a catalyst extractor and then a catalyst separator and thereafter heated in a preheater before being passed to a flash drum to remove unreacted monomers and oligomers.

EP 0 728 796 B1

PART II: EXTRUSION DEGRADATION

[0042] Referring to Figure 1, the molten polymer produced from PART I above was processed in an extrusion system which comprises a main extruder, and a side-arm extruder which is connected to the main extruder at the third stage of the main extruder.

[0043] The main extruder, manufactured by Black Clawson, is a 250 mm (10 inch) diameter three-stage single screw extruder about 915 cm (360 inches) in length having 10 heating zones. The single screw is manufactured by Berstorff. The extrusion was conducted at 30-40 RPM at an extrusion rate of 32 kg/hr/rpm 70 lbs/hr/rpm, die pressure from about 1,896 kPa (275 psi, 19 kg/cm²) to about 2,241 kPa (325 psi, 23 kg/cm²). In the main extruder, the temperatures are set as follows:

Zones 1-5 : about 154-160°C (310-320°F)
Zones 6-10: about 138°C (280°F)

[0044] It is to be noted that the above temperature is an average temperature set at the barrel of the screw. However the temperature of the molten polymer can be significantly higher from shear heating and cracking reaction. The operation of the main extruder consists of three stages. The temperature of the polymer melt can be e.g. about 177-232°C (350-450°F). Each stage includes a feed section, then a compression section, and then a metering section,

First stage: Zones 1-3
Second stage: Zones 4-6
Third stage: Zones 7-10

[0045] The butene-1-ethylene copolymer from Part I was fed to the feed section of the first stage of the main extruder. The peroxide LUPERSOL™ 101 (2,5-dimethyl-2,5-di(t-butylperoxy)hexane), manufactured by Atochem was added into the extruder at the metering zone of the first stage at about 83ℓ (22 gallon) (83ℓ) per hour, thereby forming a polymer melt having about 3000 ppm by weight of peroxide, based on the total weight of the polymer and the peroxide in the polymer melt.

[0046] The molten polymer is cracked during extrusion by the peroxide to form polymers with lower molecular weight and volatile peroxide by-products including acetone, t-butyl alcohol, formaldehyde, etc. The volatile by-products, butene-1 monomers, and a portion of the peroxide are vented from the vents available at the last portion of the first stage and the second stage.

[0047] The total residence time of the polymer melt in the main extruder is about 3-5 minutes.

[0048] The polymer is cracked in the second stage of the screw extruder to the target melt index about 190 to about 250 dg/min monitored with an on-line melt flow meter located immediately after the third stage and before the die. The melt flow of the products was adjusted to meet target melt viscosity and/or melt index by changing the temperature in the main extruder.

PART III : MASTERBATCH AND SIDE-ARM EXTRUDER

[0049] A butene-1-ethylene copolymer, known as DP8310 produced by Shell Oil Company having melt index of about 3 dg/min is mixed with a sufficient amount of LUPERSOL™ 101 in a drum to form a masterbatch containing 20,000 ppm by weight of the peroxide, based on the total weight of the masterbatch of the polymer and the peroxide. The masterbatch is fed to the side-arm extruder.

[0050] The side-arm extruder is a Black Clawson 110 mm (4½ inch) diameter extruder, 343 cm (135 inches) in length. It serves to melt and pump the masterbatch into the third stage of the main extruder. The extruder has 6 heating zones and is operated at 80-90 RPM with the temperatures set as following:

Zones 1-4: about 149°C (300°F)
Zone 5 : about 154°C (310°F)
Zone 6 : about 160°C (320°F)

[0051] The total residence time of the masterbatch in the side arm extruder is from about 30 to about 60 seconds. The temperature of the masterbatch in the side-arm extruder is about 171-182°C (340-360°F).

PART IV: ADDITION OF MASTERBATCH TO MAIN EXTRUDER

[0052] The masterbatch exiting the side-arm extruder is fed to the compression zone in the third stage of the screw

EP 0 728 796 B1

of the main extruder, which is about 30-60 seconds from the end of the extruder. The masterbatch is mixed with the polymer in the main extruder in about 1:5 ratio, thereby forming a polymeric melt having about 3200 ppm of unreacted peroxide, based on the total weight of the end product mixture.

[0053] A Melt Flow Meter was used to monitor the viscosity change at the end of the third stage. The total residence time of the polymer in the main extruder is from about 3 to about 5 minutes.

PART V: UNDERWATER PELLETIZATION

[0054] The molten polymer from the extruder is fed to a pelletizer in which the polymer flows through the holes of the die plate and cut by knives into approximately 3.2 mm (1/8 inch) diameter pellets, which are immediately quenched by chill water (16°C [60°F] or below) in the crystallization tank having an external pelletizing aid, Acumist® B12 a 10 micron high density polyethylene powder, in the water.

PART VI: PROPERTIES OF THE PELLETS

[0055] The run lasted for 9 hours without any upset from extruder or pelletizer. This is a significant improvement over the prior art process which rarely can run continuously for longer than 2 hours without upset. The viscosities of off-line samples of pellets produced from 5 lots were measured with a Brookfield Viscometer using ASTM D2556 as following:

177°C (350°F) [Pa.s] (cps)	135°C 275°F [Pa.s] (cps)
8.8 (8,800)	592 (592,000)
6.8 (6,800)	324 (324,000)
8.7 (8,700)	332 (332,000)
7.2 (7,200)	464 (464,000)
7.6 (7,600)	483 (483,000)

The viscosity specification of the pellets are as follows:

	Target	Acceptable Range
177°C (350°F)	8.5 Pa.s (8,500 cps)	6.5-105 Pa.s (6,500-105,000 cps)
135°C (275°F)	390 Pa.s (390,000 cps)	200-500 Pa.s (200,000-500,000 cps)

ILLUSTRATIVE EMBODIMENT II

[0056] Approximately 213096 kg (469,798 pounds) of butene-1-ethylene copolymer having the same composition and properties as described in Illustrative Embodiment I above was extrusion pelletized using the same equipment and similar conditions as described in Illustrative Embodiment I. The main extruder was operated at about 30-40 rpm and about 1020-1402 kg/hr (2250-3090 lbs/hr). The temperatures readings and settings of the heating zones were as follows:

Zone #	Zone Temperature Setting °C (°F)	Actual Zone Temperature		
		Reading °F	°C	°F
1	93 (200) (93°C)	289-313	143-156	(289-313)
2	93 (200)	255-314	124-157	(255-314)
3	93 (200)	335-360	168-182	(335-360)
4	138 (280) (138°C)	267-310	131-154	(267-310)
5	138 (280)	280-310	138-154	(280-310)
6	138 (280)	300-323	149-162	(300-323)
7	138 (280)	280-288	138-142	(280-288)
8	138 (280)	265-300	129-149	(265-300)
9	138 (280)	279-289	137-143	(279-289)
10	138 (280)	296-317	147-158	(296-317)

EP 0 728 796 B1

The viscosity of the off line pellets samples taken after the crystallization tank are as follows:

177°C (350°F) [Pa.s] (CPS)	135°C (275°F) [Pa.s] (cps)
10.5 (10,500)	268 (268,000)
10.5 (10,500)	210 (210,000)
10.7 (10,700)	242 (242,000)
11.4 (11,400)	158 (158,000)
9.5 (9,500)	220 (220,000)
6.8 (6,800)	239 (239,000)
8.2 (8,200)	218 (218,000)

[0057] The masterbatch extruder extrusion rate is from about 74 kg/hr (163 lbs/hr) to about 154 kg/hr (340 lbs/hr). The pellets produced contain about 3200 unreacted peroxide.

[0058] The properties of the products produced are summarized in TABLE 2. As used herein, prime products are products which fully meet the shipping and blending specifications. The recoverable rejects are products outside of shipping specification which can be reprocessed (e.g. re-cracked). Non-recoverable rejects are products outside of blending specification, e.g. viscosity too low, and reprocessing would not make it meet the specification.

COMPARATIVE EMBODIMENT

[0059] Butene-1-ethylene copolymer having the same composition and properties as described in Illustrative Example I was extrusion pelletized using the same equipment and peroxide, under similar conditions as described above, with the exception that no 5 side-arm extruder was used, and all 6000 ppm of the peroxide was added to the main extruder at stage 1. No additional peroxide was added at the third stage. The breakdown of prime products, recoverable rejects and non-recoverable rejects are listed in TABLE 2 below.

TABLE 2

CLASSIFICATION	COMPARATIVE [%]	ILLUSTRATIVE EMBODIMENT II [%]
PRIME	20.7	71.8
RECOVERABLE	9.0	16.6
NON-RECOVERABLE	70.3	11.6
TOTAL	100.0	100.0

[0060] As illustrated in TABLE 2, the process of Illustrative Embodiment II of the present invention made 71.8% of prime product, whereas the prior art process of the Comparative Example only made 20.7% prime product. The improvement in prime product is over 250% using the process of the present invention.

Claims

1. A process for making polymer pellets comprising unreacted free radical generator which can be degraded upon thermal treatment to form an olefin polymer having a melt viscosity not exceeding about 300 Pa.s (300,000 centipoise (cps)) measured by Brookfield Viscometer using ASTM D2556 at 177°C (350°F), which process comprises:

- (1) feeding an olefin polymer feedstock having a melt index of from about 0.1 to about 100 dg/minute measured by ASTM 1238 Condition E at 190°C and 2.16 g wt to a main extruder
- (2) determining the amount (x) of free radical generator required to degrade said polyolefin from step (1) in said main extruder, under the temperature(s) and residence time existing in said main extruder, to a polymer having a viscosity which is (i) sufficiently high to allow easy pelletization by pelletizer into tractable uniform non-sticky pellets with less than 5 wt% pellet agglomerates, and (ii) sufficiently low to allow blending without causing mechanical breakdowns of the mixing device by end user of the pellets;
- (3) determining amount of loss (y) of unreacted free radical generator during extrusion;
- (4) determining the total amount (z) of free radical generator required for degradation and loss in the main

extruder by adding the amount (x) to the amount (y), wherein $z=x+y$;

(5) adding said free radical generator in an amount from about 0.7 z to about 1.2 z either to (i) the first one-half section of the main extruder or (ii) said polymeric feedstock to form a first mixture;

(6) cracking said first mixture in said main extruder under heat;

(7) adding a second mixture comprising (i) from about 0.1 to about 100 wt% of a free radical generator, and (ii) from about 0 to about 99.9 wt% of said polymeric feedstock into the second half section of the main extruder to form a third mixture;

(8) passing said third mixture exiting the end of the main extruder to a pelletizer to form pellets;

wherein said second mixture is added in step (7) in an amount which provides sufficient unreacted free radical generator in the pellets produced from step (8) for subsequent decomposition and cracking of the polymer in the pellets to form a polymer having from about 0.5 Pa.s (500 cps) to about 300 Pa.s (300,000 cps), and

wherein the half life of the free radical generator used in step (5) is within about 0.1-1.0 times the half life of the free radical generator used in step (7).

2. The process according to claim 1, wherein the free radical generator used in step (5) is the same as that used in step (7).
3. The process according to claim 1 or 2, wherein said second mixture is passed through a side-arm extruder prior to the addition to said main extruder.
4. The process according to claim 1 or 2, wherein said second mixture is added to said main extruder through an injection port.
5. The process according to any one of claims 1 to 4, wherein said main extruder comprises at least one vent at a position after the addition of said free radical generator in step (5) and prior to the addition of said second mixture in step (7).
6. The process according to any one of claims 1 to 5, wherein over 70% of said free radical generators added in step (5) is decomposed and/or lost through vent before reaching the exit of the main extruder.
7. The process according to any one of the preceding claims, wherein said polyolefin in said pellets produced has a viscosity from about 50 Pa.s (50,000 cps) to about 500 Pa.s (500,000 cps) measured at 135°C (275°F) using ASTM D2556 and from about 0.5 Pa.s (500 cps) to about 300 Pa.s (300,000 cps) measured at 177°C (350°F) using ASTM D2556.
8. The process according to any one of the preceding claims, wherein said free radical generator is t-butylperoxy-maleic acid, OO-t-butyl O-isopropyl monoperoxy carbonate, OO-t-butyl O-(2-ethoxyl) monoperoxy carbonate, 2,5-dimethyl 2,5-di(benzoyl-peroxy) hexane, OO-t-amyl O-(2-ethylhexyl), mono peroxy carbonate, t-butylperoxy acetate, t-amylperoxy acetate, t-butylperoxy benzoate, t-amylperoxy benzoate, di-t-butyl diperoxyphthalate, di-cumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy) hexane, t-butyl cumyl peroxide, α - α -bis(t-butylperoxy) diisopropylbenzene, di-t-butyl peroxide, 2,5-dimethyl-2,5-di (t-butylperoxy) hexyne-3, n-butyl-4,4-bis (t-butylperoxy) valerate, 1,1-di(t-butylperoxy) 3, 3, 5- trimethyl cyclohexane, 1,1-di(t-butylperoxy) cyclohexane, 1,1-di-(t-amylperoxy) cyclohexane, 2,2-di (t-butylperoxy)butane, ethyl-3,3,-di (t-butylperoxy)butyrate, 2,2-di (t-amylperoxy) propane or ethyl 3,3-di(t-amylperoxy) butyrate, or a mixture thereof.
9. The process according to any one of the preceding claims, wherein said polyolefin is a propylene homopolymer.
10. The process according to any one of the preceding claims 1 to 8, wherein said polyolefin is a polypropylene copolymer.
11. The process according to any one of the preceding claims 1 to 8, wherein said polyolefin is a 1-butene homopolymer.
12. The process according to any one of the preceding claims 1 to 8, wherein said polyolefin is a 1-butene copolymer.
13. The process according to any one of the preceding claims 1 to 8, wherein said polyolefin is a 1-butene-ethylene copolymer.

14. The process according to any one of the preceding claims 1 to 8, wherein said polyolefin is a 1-butene-propylene copolymer.

15. The process according to any one of the preceding claims 1 to 8, wherein said polymeric feedstock comprises is blend comprising propylene homopolymer or copolymer and butene-1 homopolymer or copolymer.

16. The process according to claim 15, wherein said blend further comprises less than about 25 wt% of ethylene homopolymer or copolymer.

17. A process according to any one of claims 1 to 8 for making polymer pellets comprising unreacted 2,5-dimethyl-2,5-di(t-butylperoxy) hexane which can be degraded upon thermal treatment to form a butene-1-ethylene copolymer having a melt viscosity measured by Brookfield Viscometer using ASTM D2556 at 177°C (350°F) of from about 3 Pa.s (3,000 cps) to about 150 Pa.s (150,000 cps), which process comprises the steps of:

- (1) feeding a polymeric feedstock comprising a butene-1-ethylene copolymer comprising (i) from about 92 wt% to about 98 wt% of butene-1 and (ii) from about 2 wt% to about 8 wt% of ethylene, having a melt index of from about 0.1 to about 3.0 dg/min measured by ASTM 1238 Condition E at 190°C and 2.16 g wt to a main extruder through a feeding device, wherein the total residence time for the polymeric feedstock in the main extruder from the feeding device to the end of the main extruder is from about 2 minutes to about 6 minutes;
- (2) adding from about 800 to about 3500 ppm of 2,5-dimethyl-2,5-di(t-butylperoxy) hexane to said polymeric feedstock (i) into about first one third section of the main extruder, or (ii) prior to the feeding of said polymeric feedstock to said extruder to form a first mixture;
- (3) cracking said first mixture in the main extruder under heat;
- (4) adding a second mixture comprising (i) from about 0.1 wt% to about 100 wt% of 2,5-dimethyl-2,5-di(t-butylperoxy) hexane and (ii) from about 0 to about 99.9 wt% of said polymeric feedstock, into last one third section of the main extruder to form a third mixture;
- (5) passing said third mixture exiting the end of the main extruder to a pelletizer to form pellets;

wherein said butene-1-ethylene copolymer in said polymer pellets has a viscosity of from about 200 Pa.s (200,000 cps) to about 500 Pa.s (500,000 cps) measured at 135°C (275°F) using ASTM D2556 and from about 3 Pa.s (3,000 cps) to about 150 Pa.s (150,000 cps) measured at 177°C (350°F) using ASTM D2556; and

wherein said second mixture in step (4) is added to the main extruder in such amount that the polymer pellets produced comprises from about 2900 to 3500 ppm of unreacted peroxide.

18. The process according to claim 17, wherein said ultra low melt viscosity butylene-1-ethylene copolymer has a viscosity of from about 6.5 Pa.s (6,500 cps) to about 105 Pa.s (105,000 cps) measured by Brookfield Viscometer using ASTM D2556 at 177°C (350°F).

Patentansprüche

1. Verfahren zur Herstellung von Polymerpellets, umfassend eine nicht umgesetzte freie Radikale liefernde Substanz, die durch Wärmebehandlung abgebaut werden kann zur Bildung eines Olefinpolymers mit einer Viskosität der Schmelze, die ungefähr 300 Pa.s (300 000 Centipoise (cps)), gemessen mit einem Brookfield-Viskosimeter unter Anwendung von ASTM D2556 bei 177°C (350°F), nicht übersteigt, wobei das Verfahren umfaßt:

- (1) Einspeisen eines Ausgangsolefinpolymers mit einem Schmelzindex von etwa 0,1 bis etwa 100 dg/min, gemessen nach ASTM 1238, Bedingung E bei 190°C und 2,16 g Gewicht, in einen Hauptextruder;
- (2) Bestimmen der Menge (x) der freie Radikale liefernden Substanz, die erforderlich ist, um das Polyolefin aus Stufe (1) in dem Hauptextruder unter der bzw. den Temperatur(en) und der Verweilzeit, die in dem Hauptextruder bestehen, zu einem Polymer mit einer Viskosität abzubauen, die (i) ausreichend hoch ist, um eine leichte Pelletisierung durch eine Pelletisiervorrichtung zu leicht bearbeitbaren, gleichförmigen, nicht-klebrigen Pellets mit weniger als 5 Gew.-% Pelletagglomeraten zu erlauben, und (ii) ausreichend niedrig ist, um ein Vermischen zu erlauben, ohne mechanische Störungen der Mischvorrichtung bei dem Endverbraucher der Pellets hervorzurufen;
- (3) Bestimmen der Verlustmenge (y) von nicht umgesetzter freie Radikale liefernder Substanz während des Extrudierens;
- (4) Bestimmen der Gesamtmenge (z) der freie Radikale liefernden Substanz, die erforderlich ist zum Abbau

und Verlust in dem Hauptextruder durch Addieren der Menge (x) und der Menge (y), wobei $z=x+y$ ist;
 (5) Zugeben der freie Radikale liefernden Substanz in einer Menge von 0,7 z bis etwa 1,2 z entweder zu (i) dem ersten halben Teilabschnitt des Hauptextruders oder (ii) dem polymeren Ausgangsmaterial zur Bildung eines ersten Gemisches;

(6) Spalten des ersten Gemisches in dem Hauptextruder unter Wärme;

(7) Zugeben eines zweiten Gemisches, umfassend (i) etwa 0,1 bis etwa 100 Gew.-% einer freie Radikale liefernden Substanz und (ii) etwa 0 bis etwa 99,9 Gew.-% des polymeren Ausgangsmaterials in den zweiten halben Teilabschnitt des Hauptextruders zur Bildung eines dritten Gemisches;

(8) Führen des dritten Gemisches, das am Ende des Hauptextruders austritt, in eine Pelletisiervorrichtung zur Bildung von Pellets;

wobei das zweite Gemisch in Stufe (7) in einer Menge zugesetzt wird, die ausreichend nicht umgesetzte freie Radikale liefernde Substanz in den in Stufe (8) gebildeten Pellets zur Verfügung stellt zur anschließenden Zersetzung und zum Spalten des Polymers in den Pellets zur Bildung eines Polymers mit etwa 0,5 Pa·s (500 cps) bis etwa 300 Pa·s (etwa 300 000 cps) und

wobei die Halbwertszeit der freie Radikale liefernden Substanz, die in Stufe (5) verwendet wird, im Bereich von dem etwa 0,1- bis 1,0-fachen der Halbwertszeit der in Stufe (7) verwendeten freie Radikale liefernden Substanz liegt.

2. Verfahren nach Anspruch 1, wobei die freie Radikale liefernde Substanz, die in Stufe (5) verwendet wird, die gleiche ist wie die in Stufe (7) verwendete.
3. Verfahren nach Anspruch 1 oder 2, wobei das zweite Gemisch durch einen Seitenarmextruder geführt wird, bevor es dem Hauptextruder zugesetzt wird.
4. Verfahren nach Anspruch 1 oder 2, wobei das zweite Gemisch durch eine Einspritzöffnung in den Hauptextruder zugesetzt wird.
5. Verfahren nach einem der Ansprüche 1 bis 4, wobei der Hauptextruder mindestens eine Entlüftungsöffnung an einer Position nach der Zugabe der freie Radikale liefernden Substanz in Stufe (5) und vor der Zugabe des zweiten Gemisches in Stufe (7) umfaßt.
6. Verfahren nach einem der Ansprüche 1 bis 5, wobei über 70 % der freie Radikale liefernden Substanzen, die in Stufe (5) zugesetzt werden, zersetzt werden und/oder durch die Entlüftungsöffnung verlorengehen, bevor sie den Ausgang des Hauptextruders erreichen.
7. Verfahren nach einem der vorangehenden Ansprüche, wobei das Polyolefin in den gebildeten Pellets eine Viskosität von etwa 50 Pa·s (50 000 cps) bis etwa 500 Pa·s (500 000 cps), gemessen bei 135°C (275°F) nach ASTM D2556, und von etwa 0,5 Pa·s (500 cps) bis etwa 300 Pa·s (300 000 cps), gemessen bei 177°C (350°F) nach ASTM D2556, aufweist.
8. Verfahren nach einem der vorangehenden Ansprüche, wobei die freie Radikale liefernde Substanz tert.-Butylperoxymaleinsäure, OO-tert.-Butyl-O-isopropyl-monoperoxycarbonat, OO-tert.-Butyl-O-(2-ethoxyl)-monoperoxycarbonat, 2,5-Dimethyl-2,5-di(benzoylperoxy)-hexan, OO-tert.-Amyl-O-(2-ethylhexyl)-monoperoxycarbonat, tert.-Butylperoxyacetat, tert.-Amylperoxyacetat, tert.-Butylperoxybenzoat, tert.-Amylperoxybenzoat, Di-tert.-butyl-diperoxyphthalat, Dicumylperoxid, 2,5-Dimethyl-2,5-di(tert.-butylperoxy)hexan, tert.-Butylcumylperoxid, α - α -Bis(tert.-butylperoxy)diisopropylbenzol, Di-tert.-butylperoxid, 2,5-Dimethyl-2,5-di(tert.-butylperoxy)hexin-3, n-Butyl-4,4-bis(tert.-butylperoxy)valerat, 1,1-Di(tert.-butylperoxy)-3,3,5-trimethylcyclohexan, 1,1-Di(tert.-butylperoxy)cyclohexan, 1,1-Di(tert.-amylperoxy)cyclohexan, 2,2-Di(tert.-butylperoxy)butan, Ethyl-3,3-di(tert.-butylperoxy)butyrat, 2,2-Di(tert.-amylperoxy)propan oder Ethyl-3,3-di(tert.-amylperoxy)butyrat oder ein Gemisch davon ist.
9. Verfahren nach einem der vorangehenden Ansprüche, wobei das Polyolefin ein Propylen-Homopolymer ist.
10. Verfahren nach einem der vorangehenden Ansprüche 1 bis 8, wobei das Polyolefin ein Polypropylen-Copolymer ist.
11. Verfahren nach einem der vorangehenden Ansprüche 1 bis 8, wobei das Polyolefin ein 1-Buten-Homopolymer ist.
12. Verfahren nach einem der vorangehenden Ansprüche 1 bis 8, wobei das Polyolefin ein 1-Buten-Copolymer ist.

EP 0 728 796 B1

13. Verfahren nach einem der vorangehenden Ansprüche 1 bis 8, wobei das Polyolefin ein I-Buten-Ethylen-Copolymer ist.

14. Verfahren nach einem der vorangehenden Ansprüche 1 bis 8, wobei das Polyolefin ein 1-Buten-Propylen-Copolymer ist.

15. Verfahren nach einem der vorangehenden Ansprüche 1 bis 8, wobei das polymere Ausgangsmaterial ein Gemisch, umfassend Propylen-Homopolymer oder -Copolymer und Buten-1-Homopolymer oder -Copolymer, umfaßt.

16. Verfahren nach Anspruch 15, wobei das Gemisch zusätzlich weniger als etwa 25 Gew.-% Ethylen-Homopolymer oder -Copolymer umfaßt.

17. Verfahren nach einem der Ansprüche 1 bis 8 zur Herstellung von Polymerpellets, umfassend nicht umgesetztes 2,5-Dimethyl-2,5-di(tert.-butylperoxy)hexan, das durch Wärmebehandlung abgebaut werden kann zur Bildung eines 1-Buten-Ethylen-Copolymers mit einer Viskosität der Schmelze, gemessen mit einem Brookfield-Viskosimeter unter Anwendung von ASTM D2556 bei 177°C (350°F), von etwa 3 Pa-s (3 000 cps) bis etwa 150 Pa-s (150 000 cps), wobei das Verfahren die Stufen umfaßt:

(1) Einspeisen eines polymeren Ausgangsmaterials, umfassend ein I-Buten-Ethylen-Copolymer, umfassend (i) etwa 92 bis etwa 98 Gew.-% 1-Buten und (ii) etwa 2 bis etwa 8 Gew.-% Ethylen, mit einem Schmelzindex von etwa 0,1 bis etwa 3,0 dg/min, gemessen nach ASTM 1238, Bedingung E bei 190°C und 2,16 g Gewicht, in einen Hauptextruder durch eine Einspeisvorrichtung, wobei die Gesamtverweilzeit für das polymere Ausgangsmaterial in dem Hauptextruder von der Einspeisvorrichtung bis zu dem Ende des Hauptextruders etwa 2 min bis etwa 6 min beträgt;

(2) Zugeben von etwa 800 bis etwa 3 500 ppm 2,5-Dimethyl-2,5-di(tert.-butylperoxy)hexan zu dem polymeren Ausgangsmaterial (i) in etwa dem ersten Drittel des Hauptextruders oder (ii) vor dem Einspeisen des polymeren Ausgangsmaterials in den Extruder zur Bildung eines ersten Gemisches;

(3) Spalten des ersten Gemisches in dem Hauptextruder unter Wärme;

(4) Zugeben eines zweiten Gemisches, umfassend (i) etwa 0,1 bis etwa 100 Gew.-% 2,5-Dimethyl-2,5-di(tert.-butylperoxy)hexan und (ii) etwa 0 bis etwa 99,9 Gew.-% des polymeren Ausgangsmaterials in dem letzten Drittel des Hauptextruders zur Bildung eines dritten Gemisches;

(5) Leiten des dritten Gemisches, das am Ende des Hauptextruders austritt, in eine Pelletisiervorrichtung zur Bildung von Pellets;

wobei das 1-Buten-Ethylen-Copolymer in den Polymerpellets eine Viskosität von etwa 200 Pa-s (200 000 cps) bis etwa 500 Pa-s (500 000 cps), gemessen bei 135°C (275°F) unter Anwendung von ASTM D2556, und von etwa 3 Pa-s (3 000 cps) bis etwa 150 Pa-s (150 000 cps), gemessen bei 177°C (350°F) nach ASTM D2556, aufweist; und

wobei das zweite Gemisch in Stufe (4) in den Hauptextruder in einer solchen Menge eingebracht wird, daß die erzeugten Polymerpellets etwa 2900 bis 3500 ppm des nicht umgesetzten Peroxids enthalten.

18. Verfahren nach Anspruch 17, wobei das 1-Butylen-Ethylen-Copolymer mit ultraniedriger Viskosität der Schmelze eine Viskosität von etwa 6,5 Pa-s (6 500 cps) bis etwa 105 Pa-s (105 000 cps), gemessen mit einem Brookfield-Viskosimeter unter Anwendung von ASTM D2556 bei 177°C (350°F), aufweist.

Revendications

1. Procédé pour fabriquer des pastilles de polymère, comprenant un générateur de radicaux libres n'ayant pas réagi, qui peut être dégradé lors d'un traitement thermique pour former un polymère d'oléfine présentant une viscosité à l'état fondu qui ne dépasse pas environ 300 Pa.s (300 000 centipoise (cps)), mesurée par un viscosimètre Brookfield selon la norme ASTM D2556 à 177 °C (350 °F), lequel procédé comprend :

(1) l'alimentation d'une extrudeuse principale en charge d'alimentation de type polymère d'oléfine présentant un indice de fluidité à chaud allant d'environ 0,1 à environ 100 dg/min, mesuré selon la norme ASTM 1238-condition E à 190 °C et pour une charge de 2,16 g,

(2) la détermination de la quantité (x) de générateur de radicaux libres nécessaire pour dégrader ladite polyoléfine de l'étape (1) dans ladite extrudeuse principale, à la température ou aux températures et pour un temps

de séjour existant dans ladite extrudeuse principale, en un polymère présentant une viscosité qui est (i) suffisamment élevée pour que l'on puisse facilement le mettre sous forme de pastilles uniformes non collantes et étirables, présentant moins de 5 % en poids de pastilles agglomérées, au moyen d'une pastilleuse, et (ii) suffisamment faible pour qu'un utilisateur final des pastilles puisse les mélanger sans provoquer de pannes mécaniques du dispositif de malaxage ;

(3) la détermination de la quantité de perte (y) du générateur de radicaux libres n'ayant pas réagi, au cours de l'extrusion ;

(4) la détermination de la quantité totale (z) de générateur de radicaux libres nécessaire pour la dégradation et la perte dans l'extrudeuse principale en ajoutant la quantité (x) à la quantité (y), z étant égal à $x+y$;

(5) l'addition dudit générateur de radicaux libres en une quantité allant d'environ 0,7.z à environ 1,2.z, soit à (i) la première moitié de l'extrudeuse principale, soit à (ii) ladite charge d'alimentation polymérique pour former un premier mélange ;

(6) le craquage thermique dudit premier mélange dans ladite extrudeuse principale ;

(7) l'addition d'un second mélange comprenant (i) d'environ 0,1 à environ 100 % en poids d'un générateur de radicaux libres, et (ii) d'environ 0 à environ 99,9 % en poids de ladite charge d'alimentation polymérique, dans la seconde moitié de l'extrudeuse principale pour former un troisième mélange ;

(8) le passage dudit troisième mélange sortant de l'extrudeuse principale vers une pastilleuse pour former des pastilles ;

dans lequel on ajoute ledit second mélange dans l'étape (7) en une quantité qui donne suffisamment de générateur de radicaux libres, n'ayant pas réagi, dans les pastilles produites dans l'étape (8) pour une décomposition et un craquage ultérieurs du polymère des pastilles afin de former un polymère présentant une viscosité allant d'environ 0,5 Pa.s (500 cps) à environ 300 Pa.s (300 000 cps), et dans lequel le temps de demi-vie du générateur de radicaux libres utilisé dans l'étape (5) est égal à environ 0,1 à 1,0 fois le temps de demi-vie du générateur de radicaux libres utilisé dans l'étape (7).

2. Procédé selon la revendication 1, dans lequel le générateur de radicaux libres utilisé dans l'étape (5) est le même que celui utilisé dans l'étape (7).

3. Procédé selon la revendication 1 ou 2, dans lequel on fait passer ledit second mélange à travers une extrudeuse auxiliaire avant de l'ajouter à ladite extrudeuse principale.

4. Procédé selon la revendication 1 ou 2, dans lequel on ajoute ledit second mélange à ladite extrudeuse principale à travers un orifice d'injection.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ladite extrudeuse principale comprend au moins un événement qui se trouve après l'addition dudit générateur de radicaux libres dans l'étape (5) et avant l'addition dudit second mélange dans l'étape (7).

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel plus de 70 % desdits générateurs de radicaux libres ajoutés dans l'étape (5) sont décomposés et/ou perdus à travers l'événement avant de parvenir à la sortie de l'extrudeuse principale.

7. Procédé selon l'une quelconque des précédentes revendications, dans lequel ladite polyoléfine dans lesdites pastilles produites présente une viscosité allant d'environ 50 Pa.s (50 000 cps) à environ 500 Pa.s (500 000 cps), mesurée à 135 °C (275 °F) selon la norme ASTM D2556, et une viscosité allant d'environ 0,5 Pa.s (500 cps) à environ 300 Pa.s (300 000 cps) mesurée à 177 °C (350 °F) selon la norme ASTM D2556.

8. Procédé selon l'une quelconque des précédentes revendications, dans lequel ledit générateur de radicaux libres est l'acide t-butylperoxymaléique, le monoperoxy carbonate d'OO-t-butyle et d'O-isopropyle, le monoperoxy carbonate d'OO-t-butyle et d'O-2-éthoxyle, le 2,5-diméthyl-2,5-di(benzoylperoxy)hexane, le monoperoxy carbonate d'OO-t-amyle et d'O-2-éthylhexyle, le peroxyacétate de t-butyle, le peroxyacétate de t-amyle, le peroxybenzoate de t-butyle, le peroxybenzoate de t-amyle, le diperoxyphthalate de di-tert-butyle, le peroxyde de dicumyle, le 2,5-diméthyl-2,5-di(t-butylperoxy)hexane, le peroxyde de t-butyle et de cumyle, l' α,α -bis(t-butylperoxy)diisopropylbenzène, le peroxyde de di-t-butyle, le 2,5-diméthyl-2,5-di(t-butylperoxy)hexyne-3, le 4,4-bis(t-butylperoxy)valérate de n-butyle, le 1,1-di(t-butylperoxy)-3,3,5-triméthylcyclohexane, le 1,1-di(t-butylperoxy)cyclohexane, le 1,1-di(t-amylperoxy)cyclohexane, le 2,2-di(t-butylperoxy)butane, le 3,3-di(t-butylperoxy)butyrate d'éthyle, le 2,2-di(t-amylperoxy)propane ou le 3,3-di(t-butylperoxy)butyrate d'éthyle, ou un mélange de ces derniers.

EP 0 728 796 B1

9. Procédé selon l'une quelconque des précédentes revendications, dans lequel ladite polyoléfine est un homopolymère de propylène.
- 5 10. Procédé selon l'une quelconque des précédentes revendications 1 à 8, dans lequel ladite polyoléfine est un copolymère de polypropylène.
11. Procédé selon l'une quelconque des précédentes revendications 1 à 8, dans lequel ladite polyoléfine est un homopolymère de butène-1.
- 10 12. Procédé selon l'une quelconque des précédentes revendications 1 à 8, dans lequel ladite polyoléfine est un copolymère de butène-1.
13. Procédé selon l'une quelconque des précédentes revendications 1 à 8, dans lequel ladite polyoléfine est un copolymère butène-1/éthylène.
- 15 14. Procédé selon l'une quelconque des précédentes revendications 1 à 8, dans lequel ladite polyoléfine est un copolymère butène-1/propylène.
- 20 15. Procédé selon l'une quelconque des précédentes revendications 1 à 8, dans lequel ladite charge d'alimentation polymérique comprend un mélange comprenant un homopolymère ou copolymère de propylène et un homopolymère ou copolymère de butène-1.
- 25 16. Procédé selon la revendication 15, dans lequel ledit mélange comprend en outre moins d'environ 25 % en poids d'homopolymère ou de copolymère d'éthylène.
- 30 17. Procédé selon l'une quelconque des revendications 1 à 8, pour fabriquer des pastilles de polymère comprenant le 2,5-diméthyl-2,5-di(t-butylperoxy)hexane n'ayant pas réagi qui peut être dégradé lors d'un traitement thermique pour former un copolymère butène-1/éthylène présentant une viscosité à l'état fondu, mesurée au moyen d'un viscosimètre Brookfield selon la norme ASTM D2556 à 177 °C (350 °F), allant d'environ 3 Pa.s (3 000 cps) à environ 150 Pa.s (150 000 cps), lequel procédé comprend les étapes consistant à :
 - (1) alimenter une extrudeuse principale à travers un dispositif d'alimentation, en charge d'alimentation polymérique comprenant un copolymère butène-1/éthylène qui comprend (i) d'environ 92 % en poids à environ 98 % en poids de butène-1, et (ii) d'environ 2 % en poids à environ 8 % en poids d'éthylène, qui présente un indice de fluidité à chaud d'environ 0,1 à environ 3,0 dg/min, mesuré selon la norme ASTM 1238 - condition E à 190 °C et pour une charge de 2,16 g, le temps de séjour total de la charge d'alimentation polymérique dans l'extrudeuse principale depuis le dispositif d'alimentation jusqu'à la sortie de l'extrudeuse principale se situant dans l'intervalle qui va d'environ 2 minutes à environ 6 minutes ;
 - 35 (2) ajouter d'environ 800 à environ 3500 ppm de 2,5-diméthyl-2,5-di(t-butylperoxy)hexane à ladite charge d'alimentation polymérique, (i) dans l'extrudeuse principale au niveau de son premier tiers environ, ou (ii) avant l'alimentation en ladite charge d'alimentation polymérique, de ladite extrudeuse pour former un premier mélange ;
 - 40 (3) craquer thermiquement ledit premier mélange dans l'extrudeuse principale ;
 - 45 (4) ajouter un second mélange comprenant (i) d'environ 0,1 % en poids à environ 100 % en poids de 2,5-diméthyl-2,5-di(t-butylperoxy)hexane et (ii) d'environ 0 à environ 99,9 % en poids de ladite charge d'alimentation polymérique, dans le dernier tiers de l'extrudeuse principale pour former un troisième mélange,
 - (5) faire passer ledit troisième mélange sortant de l'extrudeuse principale vers une pastilleuse pour former des pastilles ;
- 50 dans lequel ledit copolymère butène-1/éthylène dans lesdites pastilles de polymère présente une viscosité allant d'environ 200 Pa.s (200 000 cps) à environ 500 Pa.s (500 000 cps), mesurée à 135 °C (275 °F) selon la norme ASTM D2556, et une viscosité allant d'environ 3 Pa.s (3 000 cps) à environ 150 Pa.s (150 000 cps), mesurée à 177 °C (350 °F) selon la norme ASTM D2556 ; et
- 55 dans lequel on ajoute ledit second mélange dans l'étape (4) à l'extrudeuse principale en une quantité telle que les pastilles de polymère produites comprennent d'environ 2900 à 3500 ppm du peroxyde n'ayant pas réagi.
18. Procédé selon la revendication 17, dans lequel ledit copolymère butylène-1/éthylène de viscosité à l'état fondu ultrafaible présente une viscosité allant d'environ 6,5 Pa.s (6 500 cps) à environ 105 Pa.s (105 000 cps), mesurée

EP 0 728 796 B1

au moyen d'un viscosimètre Brookfield selon la norme ASTM D2556 à 177 °C (350 °F).

5

10

15

20

25

30

35

40

45

50

55

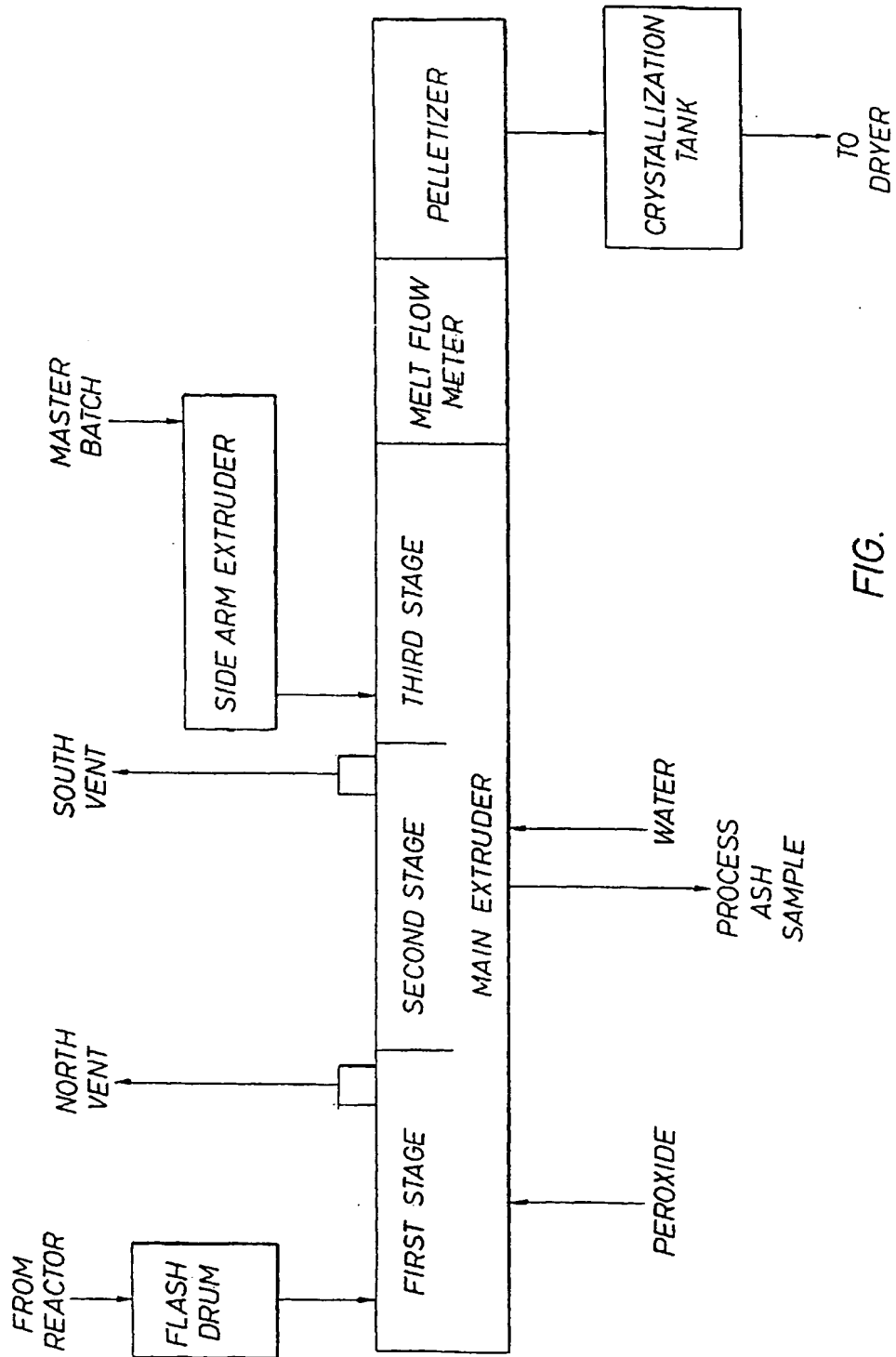


FIG.